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(54) PLASMA FILM FORMING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a method for forming an insulating film which has a rigid bond and is composed of a CF film which is difficult to be decomposed, the interlayer insulating film of a semiconductor device, for example.
SOLUTION: A C5F8 gas of a circular structure and hydrocarbon gas, C2H4 gas, for example, are used as film forming gas. The gases are made into plasma at the pressure of 0.1 Torr, for example, and a CF film is formed on a semiconductor wafer by an active species at the process temperature of 400°C. C5F8, C4F6 and C3F4 having the double bond are considered as the decomposed product of C5F8 gas. The re-bonded product has a stereoscopic structure and has the rigid bonding. Bonding is difficult to be cut even at the high temperature and degassing quantity is less.

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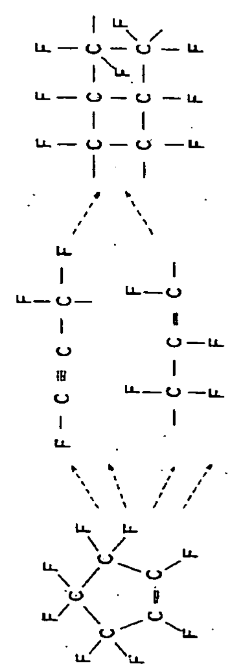
(54)【発明の名称】　プラズマ成膜方法

(57)【要約】

【課題】　ＣＦ膜を半導体デバイスの層間絶縁膜として用いようとすると、Ｗ（タングステン）の配線を形成するときに例えば４００℃～４５０℃付近にまでＣＦ膜が加熱され、このときにＦ系のガスがＣＦ膜から抜け、配線の腐食や膜減りに伴う種々の不都合が生じる。

【解決手段】　環状構造のC_5F_8ガス及び炭化水素ガス例えばC_2H_4ガスを成膜ガスとして用い、これらガスを例えば０．１Ｔｏｒｒの圧力下でプラズマ化してプロセス温度４００℃の下でその活性種により半導体ウエハ上にＣＦ膜を成膜する。C_5F_8ガスの分解生成物は二重結合をもったC_5F_8、C_4F_6、C_3F_4などと考えられ、その再結合物は立体構造で結合が強固であり、高温下でも結合が切れにくく脱ガス量が少ない。



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CLAIMS

[Claim(s)]
[Claim 1] C five F8 of cyclic structure The plasma membrane formation approach characterized by forming the insulator layer which plasma-izes the membrane formation gas containing gas, and consists of fluoridation carbon film on a processed substrate by the plasma.
[Claim 2] Membrane formation gas is C five F8. The plasma membrane formation approach according to claim 1 characterized by including at least one side of gas, and hydrocarbon gas or hydrogen gas.
[Claim 3] The plasma membrane formation approach according to claim 1 or 2 characterized by a process pressure being 5.5Pa or less [claim 4] C five F8 of straight chain structure The plasma membrane formation approach characterized by forming the insulator layer which plasma-izes the membrane formation gas containing gas, and consists of fluoridation carbon film on a processed substrate by the plasma.

[Claim 5] Membrane formation gas is C five F8. The plasma membrane formation approach according to claim 4 characterized by including at least one side of gas, and hydrocarbon gas or hydrogen gas.
[Claim 6] The plasma membrane formation approach according to claim 4 or 5 characterized by a process pressure being 0.3Pa or less [claim 7] The plasma membrane formation approach according to claim 1, 2, 3, 4, 5, or 6 characterized by the temperature on a processed substrate being 360 degrees C or more.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the approach of forming the fluoridation carbon film which can be used for the interlayer insulation film of a semiconductor device by plasma treatment.
[0002]
[Description of the Prior Art] In order to attain high integration of a semiconductor device, the device of multilayering of detailed-izing of a pattern and a circuit is advanced, and there is a technique which multilayers wiring as one of them. In order to take multilayer-interconnection structure, while connecting between the wiring layer of the n-th layer, and the wiring layers of eye watch (n+1) by the conductive layer, the thin film with which fields other than a conductive layer are called an interlayer insulation film is formed.
[0003] It is SiO2 as a typical thing of this interlayer insulation film. Although there is film, in order to attain improvement in the speed much more about actuation of a device in recent years, it is required that specific inductive capacity of an interlayer insulation film should be made low, and the examination about the construction material of an interlayer insulation film is made. Namely, SiO2 Specific inductive capacity is about 4 and the force is directed towards the excavation of construction material smaller than this. Although implementation-ization of SiOF whose specific inductive capacity is 3.5 as one of them is advanced, this invention person is observing the fluoridation carbon film (henceforth "CF film") with still smaller specific inductive capacity.
[0004]
[Problem(s) to be Solved by the Invention] It is SiO2 to which drawing 19 is a part of circuit part formed in the wafer, and 11, the conductive layer which 12 becomes from CF film, and 13 and 14W (tungsten), the conductive layer which 15 becomes from aluminum (aluminum), and 16 doped P and B. The film and 17 are n type semiconductor fields. By the way, the process temperature when forming 13 [W-layer] is 400-450 degrees C, and the CF film 11 and 12 is heated to that process temperature at this time. However, if heated by such elevated temperature, a part of C-F association will go out, and F (fluorine) system gas will mainly be desorbed from CF film. as this F system gas -- F, CF, and CF2 etc. -- it is mentioned.
[0005] Thus, if F system gas ****s, the following problems will arise.
a) Metal wiring of aluminum, a tungsten, etc. corrodes.
b) Although it also has the function for an insulator layer to hold down aluminum wiring and to prevent the wave of aluminum, holding down by the insulator layer becomes weaker with degasifying, as a result, aluminum wiring surges, and it becomes easy to generate the electric defect called electromigration.
c) A crack goes into an insulator layer and the insulation during wiring worsens, and

when the extent is large, it becomes impossible to form the wiring layer of the next step.
d) If there are many omissions of F, specific inductive capacity will increase.
[0006] This invention is made under such a situation, and the object has firm association and is to offer the approach of forming the insulator layer which consists of CF film which is hard to disassemble, for example, the interlayer insulation film of a semiconductor device.
[0007]
[Means for Solving the Problem] The plasma membrane formation approach of this invention is C five F8 of cyclic structure or straight chain structure. The membrane formation gas containing gas is plasma-ized, and it is characterized by forming the insulator layer which consists of fluoridation carbon film on a processed substrate by the plasma. In this case, membrane formation gas is C five F8. It consists at least of one side of gas, and hydrocarbon gas or hydrogen gas, the temperature of a processed substrate is set as 360 degrees C or more, and a process pressure is C five F8 of cyclic structure straight chain structure. If it is gas, it will be set as 5.5Pa or less, and it is C five F8 of straight chain structure. If it is gas, it will be set as 0.3Pa.
[0008]
[Embodiment of the Invention] An example of the plasma treatment equipment first used for the gestalt of operation of this invention is shown in drawing 1 . It has the vacuum housing 2 formed of aluminum etc., and it is made caudad open for free passage, and is connected, and this equipment consists of the 1st tubed vacuum chamber 21 which this vacuum housing 2 is located [vacuum chamber] up and generates the plasma, and this 2nd tubed vacuum chamber 22 with larger aperture than the 1st vacuum chamber 21. In addition, this vacuum housing 2 is grounded and has zero potential.
[0009] The transparency aperture 23 formed with ingredients, such as a member, for example, a quartz etc., which opening is carried out and penetrates microwave into this part, is formed airtightly, and the upper bed of this vacuum housing 2 maintains the vacua in a vacuum housing 2. The microwave which the waveguide 25 connected to the RF power supply section 24 which generates 2.45GHz microwave is formed in the outside of this transparency aperture 23, and introduced the microwave generated in the RF power supply section 24 with the waveguide 25 by the TE mode, or was guided by the TE mode can be changed into the TM mode with a waveguide 25, and it can introduce now into the 1st vacuum chamber 21 from the transparency aperture 23.
[0010] While the gas nozzle 31 uniformly arranged along that hoop direction is formed in the side attachment wall which divides the 1st vacuum chamber 21, the source of gas of Ar gas which is not illustrated, for example, a source, is connected to this nozzle 31, and Ar gas can be supplied now to the upper part in the 1st vacuum chamber 21 uniformly without nonuniformity.
[0011] In said 2nd vacuum chamber 22, the installation base 4 of a wafer is formed so that it may counter with said 1st vacuum chamber 21. This installation base 4 equips the surface section with the electrostatic chuck 41, and the RF power supply section 42 is connected to the electrode of this electrostatic chuck 41 so that the bias voltage for drawing ion in a wafer besides [which adsorbs a wafer] DC power supply (not shown) may be impressed.
[0012] On the other hand, the ring-like membrane formation gas supply section 51 is formed in the upper part 21 of said 2nd vacuum chamber 22, i.e., the 1st vacuum chamber, and a part open for free passage, and this membrane formation gas supply section 51 is constituted so that two kinds of membrane formation gas may be supplied from gas supply lines 52 and 53 and that mixed gas may be supplied in a

vacuum housing 2 from the gas hole 54 of inner skin.

[0013] the periphery of a side attachment wall which divides said 1st vacuum chamber 21 is approached at this -- making -- as magnetic field means forming -- the shape of for example, a ring -- main -- electromagnetism -- while a coil 26 is arranged -- the lower part side of the 2nd vacuum chamber 22 -- ring-like assistance -- electromagnetism -- the coil 27 is arranged. Moreover, the exhaust pipe 28 is respectively connected to the pars basilaris ossis occipitalis of the 2nd vacuum chamber 22 in the location of two places symmetrical with the medial axis of a vacuum chamber 22.

[0014] Next, how to form the interlayer insulation film which consists of CF film on the wafer W which is a processed substrate is explained using above-mentioned equipment. First, it carries in from the load lock chamber which does not illustrate the wafer W with which aluminum wiring was formed in the front face by the conveyance arm which does not open and illustrate the gate valve which was prepared in the side attachment wall of a vacuum housing 2, and which is not illustrated, and lays on the installation base 4, and electrostatic adsorption of the wafer W is carried out by the electrostatic chuck 41.

[0015] Then, after closing a gate valve and sealing the interior, while exhausting an internal ambient atmosphere, carrying out vacuum suction to a predetermined degree of vacuum and introducing the gas for plasma generating, for example, Ar gas, into the 1st vacuum chamber 21 from the plasma gas nozzle 31 from an exhaust pipe 28, membrane formation gas is introduced by the predetermined flow rate into the 2nd vacuum chamber 22 from the membrane formation gas supply section 5.

[0016] As the description is in membrane formation gas with the gestalt of this operation and here has indicated on the left-hand side of drawing 2 (a) as this membrane formation gas, it is C five F8 of cyclic structure. Gas is used. Moreover, it is hydrocarbon gas two H4, for example, C, as membrane formation gas. Gas is also used and it is C five F8. Gas and C2H4 Gas is supplied in a vacuum housing 2 through the inside of the membrane formation gas supply section 51 from the gas installation tubing 52 and 53, respectively. And while maintaining the inside of a vacuum housing 2 to predetermined process ** and impressing the bias voltage of 13.56MHz and 1500W to the installation base 4 by the RF generator section 42, the skin temperature of the installation base 4 is set as about 400 degrees C.

[0017] The 2.45GHz RF (microwave) from the RF power supply section 24 results in the head-lining section of a vacuum housing 2 through a waveguide 25, penetrates the transparency aperture 23 here, and is introduced into the 1st vacuum chamber 21. on the other hand -- the inside of a vacuum housing 2 -- electromagnetism -- the magnetic field which goes to the lower part of the 2nd vacuum chamber 22 from the upper part of the 1st vacuum chamber 21 with coils 26 and 27 is formed. For example, the strength of a magnetic field becomes 875 gauss near the lower part of the 1st vacuum chamber 21, a electron cyclotron resonance arises by the interaction of a magnetic field and microwave, and Ar gas is plasma-ized by this resonance, and it is carried out densification. The plasma style which flowed in in the 2nd vacuum chamber 22 from the 1st vacuum chamber 21 is C five F8 currently supplied here. Gas and C two H4 Gas is activated, active species is formed and CF film is formed on Wafer W. In addition, when manufacturing a actual device, it etches by the predetermined pattern to this CF film after that, for example, W film is embedded in a slot, and W wiring is formed.

[0018] CF film formed by such approach has few omissions of F, even if thermal stability is large, that is, becomes an elevated temperature so that it may have firm association and the below-mentioned experimental result may also show. As that reason is shown in drawing 2 , it is C five F8 of cyclic structure. A decomposition

product tends to make a spacial configuration, as a result, C-F association becomes firm, and even if it applies heat, it is thought that that association cannot go out easily. C five F8 of cyclic structure When the decomposition product was made to evaporate under a 0.002Pa reduced pressure ambient atmosphere and was analyzed from that of a mass spectrometer, the result shown in drawing 3 was obtained. C three F3 which is easy to form a spacial configuration from this result C four F4 It can hear about existing mostly as a pyrolysate.

[0019] It is C four F8 of cyclic structure as an example of a comparison of this example. Considering the case where gas is used as membrane formation gas, as shown in drawing 4 , it is C four F8. A decomposition product is C two F4. It is C4F8 so that, it may become easy to take straight chain structure and the below-mentioned comparison experimental result may also show for this reason. CF film formed using gas has small thermal stability.

[0020] It sets above and is C five F8 as membrane formation gas. It is C two H4 to use gas as gas added with this although it is the conditions of this invention. Not only gas but CH4 Gas and C two H6 Hydrocarbon gas, such as gas, may be used, and you may be hydrogen gas instead of hydrocarbon gas, and may be the mixed gas of hydrocarbon gas and hydrogen gas.

[0021] (Example 1) The weight change under the elevated temperature which is the index of the thermal stability of a thin film was investigated using the measuring device shown in drawing 5 here. The crucible with which a vacuum housing and 62 were hung by the heater and 63 was hung for 61 by the beam of a lightweight balance device in drawing 5 , and 64 are the gravimetry sections. About the measuring method, it put in in the end crater 63 which has failed to shave CF film on a wafer, temperature up of the temperature in a crucible 63 was carried out to 425 degrees C under the vacuum ambient atmosphere, it heated as it is for 2 hours, and weight change was investigated in the gravimetry section 64. In the membrane formation process stated with the gestalt of above-mentioned operation, the temperature at the time of membrane formation was set as seven kinds (300 degrees C, 325 degrees C, 350 degrees C, 360 degrees C, 380 degrees C, 400 degrees C, 420 degrees C, and 440 degrees C), and when weight change was investigated about CF film obtained at each process temperature, the result shown in drawing 6 was obtained.

[0022] However, C five F8 Gas and C two H4 The flow rate of gas and Ar gas is [2000W and 1500W, and the process pressure of 60sccm(s), 20sccm and 150sccm (s), microwave power (RF generator section 24), and bias power (RF generator section 4)] 0.1Pa, respectively. In addition, weight change is a value expressed with {(A-B) /A} x100, when weight of the thin film in the end crater which gets the weight of the thin film in the end crater which gets before applying heat after applying A and heat is set to B.

[0023] When process temperature is 360 degrees C so that drawing 6 may show, weight change becomes 2.8% and 3% or less, and it is understood that especially weight change is dramatically as small as 1.4% or less in the case of 400 degrees C or more, thermal stability is high, and there is little degasifying.

[0024] Moreover, it considers as 400 degrees C and, for other process conditions, process temperature is C5F8 as an above-mentioned passage. Gas and C two H4 When the flow rate of gas was changed, and investigated about weight change of obtained CF film becoming what, the result shown in drawing 7 was obtained. however, flow rate -- C5 F8 / C two H4 it is -- C five F8 The flow rate is fixed to 60sccm(s). If flow rate is 3 as this result shows, weight change is as small as 1.4% and flow rate is made small, weight change will become small almost linearly, but if it becomes lower than 1, ** will occur [the film] and membrane formation will become difficult.

[0025] Furthermore, process temperature is 400 degrees C and C five F8. Gas and C two H4 When the flow rate of gas was set to 60sccm(s) and 20sccm, respectively, and process ** was changed as the passage above-mentioned [other process conditions], and investigated about what weight change of obtained CF film becomes, the result shown in drawing 8 was obtained. If process ** is 5.5Pa or less as this result shows, weight change is as small as 2% or less.
[0026] (Example 2) It sets in the example 1 and is C two H4. Hydrogen gas (H2 gas) was used instead of gas, various process conditions were changed and the above-mentioned weight change was investigated about obtained CF film. The temperature at the time of membrane formation was first set as five kinds, 300 degrees C, 350 degrees C, 360 degrees C, 400 degrees C, and 420 degrees C, and when weight change was investigated about CF film obtained at each process temperature, the result shown in drawing 9 was obtained.
[0027] However, C five F8 Gas and H2 The flow rate of gas and Ar gas is [2000W and 1500W, and the process pressure of 60sccm(s), 40sccm and 150sccm(s), microwave power (RF generator section 24), and bias power (RF generator section 4)] 0.2Pa, respectively.
[0028] It is understood that temperature dependence is the same as that of an example 1 in general so that drawing 9 may show, weight change becomes 2.8% and 3% or less when process temperature is 360 degrees C, especially weight change is dramatically as small as 1.5% in the case of 400 degrees C or more, thermal stability is large, and there is little degasifying. In addition, when 420 degrees C was exceeded, film peeling happened and membrane formation was not completed.
[0029] Moreover, it considers as 400 degrees C and, for other process conditions, process temperature is C5F8 as an above-mentioned passage. Gas and H2 When the flow rate of gas was changed, and investigated about weight change of obtained CF film becoming what, the result shown in drawing 10 was obtained. however, flow rate -- C five F8 / H2 it is -- C five F8 The flow rate is fixed to 60sccm(s). Although membranes were not formed even if flow rate could not form membranes by film peeling less than by 0.8 but flow rate exceeded 2 on the other hand, in this range, weight change was as small as 2% or less.
[0030] Furthermore, process temperature is 400 degrees C and C five F8. Gas and H2 When the flow rate of gas was set to 60sccm(s) and 40ccm, respectively, and process ** was changed as the passage above-mentioned [other process conditions], and investigated about what weight change of obtained CF film becomes, the result shown in drawing 11 was obtained. The pressure dependency is the same as that of an example 1 in general, and if process ** is 5.5Pa or less, weight change is as small [the dependency] as 2% or less, so that this result may show.
[0031] (Example 3) Next, it is C five F8 of cyclic structure as membrane formation gas. It is C five F8 of straight chain structure instead of gas. Gas (this is indicated to be <C5 F8 gas> below) is used. The temperature at the time of membrane formation was set as seven kinds, 300 degrees C, 325 degrees C, 350 degrees C, 360 degrees C, 400 degrees C, 420 degrees C, and 440 degrees C, and when weight change was investigated about CF film obtained at each process temperature, the result shown in drawing 12 was obtained.
[0032] However, <C five F8 Gas > and C two H4 The flow rate of gas and Ar gas is [2000W and 1500W, and the process pressure of 60sccm(s), 20sccm and 150sccm (s), microwave power (RF generator section 24), and bias power (RF generator section 4)] 0.1Pa, respectively.
[0033] Although the same inclination as an example 1 is shown that drawing 12 shows temperature dependence, when process temperature is 360 degrees C, weight

change is 2.8%, and even if it makes process temperature high more than it, weight change does not change so much. even when a molecular formula is the same -- <C five F8 In gas >, weight change is over 2%, and weight change of CF film is larger than the case of five FC8 gas of cyclic structure used in the example 1. About the reason, it is C five F8 of cyclic structure. The direction of gas is considered to be what is much more easy to make a spacial configuration. However, it is lower than 3% and weight change is below-mentioned C four F8. Thermal stability is larger than gas and it is effective as membrane formation gas of CF film.

[0034] Moreover, it considers as 400 degrees C and, for other process conditions, process temperature is <C five F8 as an above-mentioned passage. Gas > and C two H4 When the flow rate of gas was changed, and investigated about weight change of obtained CF film becoming what, the result shown in drawing 1313 was obtained. however, flow rate -- <C five F8> / C two H4 it is -- <C five F8 The flow rate of gas > is fixed to 60sccm(s). It was difficult for flow rate to maintain membrane formation by film peeling less than by one.

[0035] Furthermore, process temperature is 400 degrees C and <C five F8. Gas > and C two H4 When the flow rate of gas was set to 60sccm(s) and 20ccm, respectively, and process ** was changed as the passage above-mentioned [other process conditions], and investigated about what weight change of obtained CF film becomes, the result shown in drawing 14 was obtained. If process ** is not 0.3Pa or less, as for a pressure dependency, unlike an example 1, weight change will not become 3% or less, so that this result may show. Drawing 15 is <C five F8. It is as a result of [of the mass analysis of gas >] measurement, and even if it guesses from these decomposition products, it is possible that CF film solidifies considerably and has network structure.

[0036] (Example of a comparison) Next, it is C five F8 of cyclic structure as membrane formation gas. It is C four F8 of cyclic structure instead of gas. When weight change of CF film which carried out **** membrane formation for gas was investigated, in 400 degrees C, weight change had process temperature quite as large as 3.7%. However, C four F8 Gas and C2H4 The flow rate of gas was set to 40sccm(s) and 30sccm, respectively, and process ** was set to 0.1Pa. Moreover, microwave power is set to 2700W and other conditions are the same as an example 1.

[0037] The weight change about CF film which formed process temperature as 400 degrees C in examples 1 and 3 and the example of a comparison is shown in drawing 16 . It is C four F8 so that this result may show. When gas is used, it is C five F8. Gas or <C five F8 Compared with the case where gas > is used, weight change is large. this already showed drawing 4 -- as -- C four F8 if its association of C-F is weak since CF film with which gas decomposed and was obtained by recombining has much straight chain structure, and heat is applied for this reason -- F -- beginning -- CF and CF2 etc. -- it is surmised that it is because there are many amounts of desorption. In addition, drawing 17 is C four F8. It is as a result of [of the mass analysis of gas] measurement, and is C two F4 like previous statement as a decomposition product. It turns out many.

[0038] Furthermore, it sets under the process temperature of 400 degrees C again, and is C five F8 of cyclic structure. CF film obtained using gas, and C four F8 Mass analysis under an elevated temperature was performed about CF film obtained using gas. This measurement placed the thin film of the specified quantity into the vacuum housing, heated the inside of this vacuum housing at 425 degrees C, and, specifically, the mass spectrometer linked to a vacuum housing performed it. A result is as being shown in drawing 18 (a) and (b). In this drawing, an axis of ordinate is the amount of non-dimensions corresponding to the reinforcement of a spectrum, and

the part with a peak shows desorption of each gas. Moreover, it is the time amount after starting the temperature up in a vacuum housing, an axis of abscissa performs temperature up the rate for 10-degree-C/from a room temperature, and after it amounts to 425 degrees C, it holds it for 30 minutes.

[0039] (b) whose direction of (a) which is this invention about the amount desorbed from CF film as F and HF is an example of a comparison -- markedly -- alike -- few -- moreover, CF, CF2, and CF3 It is also related and there is (less a) than (b). CF film which formed membranes using five FC8 gas of cyclic structure also from the result of this mass analysis -- association -- being strong -- thermal -- high stability -- **** -- it can observe that it is. Furthermore, this invention can be applied also when generating the plasma by the approach of giving electric field and a field to raw gas etc., from the coil wound around the container of the shape of a dome which is not restricted to generating the plasma by ECR, for example, is called ICP (Inductive Coupled Plasma) etc.

[0040]

[Effect of the Invention] As mentioned above, according to this invention, thermal stability is large and desorption of the gas of F system can generate small CF film. Therefore, if this CF film is used for the interlayer insulation film of a semiconductor device, there is no possibility of corroding metal wiring and the wave of aluminum wiring and generating of a crack can also be prevented. Since CF film attracts attention as an effective insulator layer with small specific inductive capacity while detailed-izing of a semiconductor device and improvement in the speed are demanded, this invention is an approach effective when attaining utilization as an insulator layer of CF film.

[Translation done.]